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④発明の名称 白金合金触媒とその製造方法

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## 明 細 書

## 1. 発明の名称

白金合金触媒とその製造方法

## 2. 特許請求の範囲

(1) カーボン担体上に、(i)白金、(ii)マンガン、及び(iii)ニッケル及びコバルトの少なくとも1種を担持させて成る白金合金触媒。

(2) 40~90原子%の白金、30~5原子%のマンガン及び30~5原子%のニッケル及びコバルト少なくとも1種が担持された請求項1に記載の白金合金触媒。

(3) カーボン担体を白金含有イオンの溶液に浸漬し還元剤を使用して前記白金含有イオンを白金に還元して前記カーボン担体上に析出させ、該カーボン担体上に、マンガン、及びニッケル及びコバルト少なくとも1種のそれぞれの金属の有機酸アミン塩の溶液を加えかつ前記カーボン担体上の白金と合金化することを含んで成る白金合金触媒の製造方法。

(4) 有機酸アミン塩がギ酸アミン塩及び／又は

酢酸アミン塩である請求項3に記載の製造方法。

(5) 還元剤が、チオ硫酸塩及び／又はメタ重亜硫酸塩である請求項3又は4に記載の製造方法。

## 3. 発明の詳細な説明

(産業上の利用分野)

本発明は、白金及びマンガンと他の金属をカーボン担体上へ担持させた触媒、特に燃料電池の電極触媒として使用される白金合金触媒と、その製造方法に関する。

(従来技術とその問題点)

従来から各種化学反应用触媒や燃料電池の電極触媒として、カーボン担体上に白金を主とする各種触媒金属を担持させた触媒が使用されている。そして触媒性能を向上させるために白金に他の金属例えばニッケルやクロムを添加した触媒も多数知られている。

しかしながらこれらの白金含有触媒も各種反应用触媒としての活性が十分とはいえず、より活性が高く、更に好ましくは寿命の長い触媒が望まれている。

本発明者らは、寿命が長くかつ触媒活性も比較的高い、カーボン担体上に担持した触媒金属をカーバイド化した白金合金触媒を提案した(特開平1-210035号)。該白金触媒では、担持された触媒金属がカーバイド化により担体に強く吸着されているため、前記触媒が高温反応において使用されても、各触媒金属粒子と前記担体間の結合が弱まって該粒子が移動し他の粒子と凝集して表面積の減少従って活性の低下を招くことが殆どなく長期間に亘って比較的高い触媒活性を維持できるという利点を有している。

しかしながら、この触媒は十分な寿命を有する反面、触媒金属をカーバイド化するため各金属が部分的にカーボンにより被覆されるため、触媒としての有効表面積の低下は回避できず、該低下を抑制するためには高価な白金等を過剰に使用しなければならず、単価当たりの活性という面からは必ずしも満足できるものではない。活性向上のためには従来から担持させる金属あるいはその組み合わせの選択、単位担持量当たりの活性を高める

本発明は、白金をはじめとする触媒金属にマンガンを加えることによって触媒の比活性を向上させる点を最大の特徴とする。

従来の白金のみを担持させた白金触媒に、第2金属を添加して合金させることにより、前記白金触媒の活性が向上させることができ、特に添加する第2の金属を適宜選択することにより顕著な活性向上が可能であり、更に第3の金属を添加することにより活性をより向上させることができることが多い。この添加金属としてマンガンは従来からあまり重視されていないが、本発明者らは白金と、ニッケル及びコバルトの少なくとも一方の金属を担持したカーボン担体にマンガンを追加すると活性がより向上し従来にない活性の高い白金合金触媒を提供できることを見出し、本発明に到達したものである。

本発明では触媒担体としてカーボンを使用する。該カーボンとは、カーボンブラック、グラファイト、活性炭等炭素を主成分とする単体で任意の形態を有する物質を総称する。該カーボン担体は多

ための担体上への触媒金属の高分散度の達成等が試みられている。

(発明の目的)

本発明は従来存在しない新しい触媒金属の組み合わせを選択することにより、十分満足できる触媒活性を有する白金合金触媒及びその製造方法を提供することを目的とする。

(問題点を解決するための手段)

本発明は、第1にカーボン担体上に、(i)白金、(ii)マンガン、及び(iii)ニッケル及びコバルトの少なくとも1種を担持させて成る白金合金触媒であり、第2にカーボン担体を白金含有イオンの溶液に浸漬し還元剤を使用して前記白金含有イオンを白金に還元して前記カーボン担体上に析出させ、該カーボン担体上に、マンガン、及びニッケル及びコバルト少なくとも1種のそれぞれの金属の有機酸アミン塩の溶液を加えかつ前記カーボン担体上の白金と合金化することを含んで成る白金合金触媒の製造方法である。

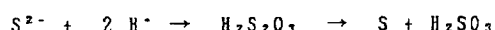
以下本発明を詳細に説明する。

孔質で大きな表面積、例えば30~2000 $\text{m}^2/\text{g}$ 程度を有し、粒径が100~5000 $\text{\AA}$ 程度であることが望ましく、例えばアセチレン・ブラック(商品名、Shawinigan Acetylene Black、デンカブラック等)や導電性カーボンブラック(商品名、VulcanXC-72等)やグラファイト化したカーボンブラック等を使用することができる。本発明では担体がカーボンであるため、後述する合金化の際の高温で各触媒金属の担体側の反応には直接関与しない部分がカーボン担体との相互作用によりカーバイド化に類似する作用を受けて前記カーボン担体と強く結合して凝集抑制の効果が生ずるものと推測することができる。

本発明方法では、まず前記カーボン担体上に白金金属を担持させる。該白金金属の担持方法は、白金含有イオンの溶液例えば塩化白金酸水溶液を前記カーボン担体に含浸させ前記白金含有イオンを還元して前記カーボン担体上に白金金属を析出させる従来法をそのまま使用することができる。しかしながら該還元方法において強い還元剤を使

用すると、生成する白金の粒径が大きくなり、単位重量当たりの表面積がかなり減少してしまう。そのため弱い還元剤である例えばチオ硫酸又はそのナトリウム塩 ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) を利用して白金の表面積減少を抑制することが好ましい。該チオ硫酸又はそのナトリウム塩は、水溶液中の前記白金含有イオンである塩化白金イオンと反応して微細に分割された高表面積の金属ゾルを生成する。

このチオ硫酸ナトリウムを使用する反応では酸性溶液中で起こることが知られている硫黄化合物の分解により生ずる非常に微細に分割された硫黄ゾルが次の式に従って生成するものと思われる。



このように生成した硫黄粒子は非常に微細に分割された金属触媒粒子の成長用核として働く。従って初めの数mlのチオ硫酸溶液はゆっくりと添加つまり滴下し、残りの溶液は一度に添加し、前記した成長用核が確実に形成されるようにすることが好ましい。

反応の進行に伴って溶液の色は黄色から橙色に

変化し、更に数時間に亘って金属微結晶が成長するに従って溶液の色は徐々に濃くなる。該溶液を通過する光はチンダル現象を示し、コロイド粒子が存在していることが分かる。

このゾルを前記カーボン担体上に吸着させ、乾燥等の適宜の操作を経て白金が担持されたカーボン担体を得ることができる。

つまり、前記溶液がほぼ不透明になったところで前記カーボン担体を加え、生成するスラリーを例えば超音波攪拌器を使用して攪拌して前記溶液相を前記カーボン担体の孔へ進入させる。この操作により濃厚なスラリーが形成され、これは懸濁のまま維持され沈殿することは殆どない。このスラリーを例えば75~80℃で1~3日乾燥して水を除去すると反応副生成物の塩を含む乾燥粉末が得られる。この乾燥した触媒を例えば100~200mlの蒸留水で数回抽出して前記副生成物を溶解させ除去することができる。グラファイト化したカーボンブラック担体の場合には、前記スラリーは沈殿し、水相を捨てることにより触媒を該水相から分離すること

ができ、これを数回繰返し、該触媒を約110℃で一晩乾燥する。

このように製造された触媒は大きな表面積を有している。例えばこの方法により、濃度が1g/100ml程度の塩化白金酸水溶液を、濃度が3g/75ml程度のチオ硫酸ナトリウム(5水塩)の水溶液と反応させると、白金の比表面積が約148m<sup>2</sup>/gで粒径の均一な白金が担持された触媒を得ることができる。

上記操作の代わりに、スラリー化—濾過—洗浄プロセスを利用することもできる。これはアセチレンブラックのような容易には沈殿しない触媒の場合に使用することができる。

このプロセスで生成する触媒粒子は、塩化白金イオンとチオ硫酸イオン間の反応の熱力学的ドライビングフォースが従来技術のものより小さく、より欠陥の少ない微結晶粒子が生成するため、白金の表面積が使用時間に従って減少してしまう粒子成長に対してより大きな耐性があると考えられる。前記したチオ硫酸塩と塩化白金酸間の反応に

より20Å以下の均一粒径の微細な粒子が得られる。

上記したチオ硫酸ナトリウム以外に本発明方法で使用できる比較的弱い還元剤として、メタ重亜硫酸ナトリウム( $\text{Na}_2\text{S}_2\text{O}_5$ )等がある。

これまで本発明方法で使用されるカーボン担体に白金含有溶液を含浸させた後に白金含有イオンを還元する方法につき詳述したが、本発明に係わる白金合金触媒はこれとは逆に含浸前に前記白金含有イオンを還元して製造した触媒であってもよく、この方法によっても高分散度の触媒粒子を得ることができる。

次いで前記白金を担持させたカーボン担体上に白金以外の金属つまりマンガン及び、コバルト、ニッケルの少なくとも一方を担持させ、更に白金と他の金属を加熱して合金化するが、高温で合金すると生ずる合金が凝集して表面積が減少するため通常の合金化方法を採用することは好ましくない。そのため本発明方法では、まず前記白金に添加すべき金属つまりマンガ、コバルト及び/又はニッケルの有機酸塩好ましくはギ酸塩又は酢酸

塩の温水溶液中に水酸化アンモニウムを加えて有機酸アミン金属塩好ましくはギ酸アミン又は酢酸アミンの金属塩に変換する。

従来の一般的金属塩(例えば硝酸塩など)を熱処理した場合には、耐熱性酸化物を生成し、白金と合金化させるための還元に高温を必要とし、その結果白金が合金化される前に結晶子の成長(表面積の低下)を引き起こしてしまうが、本発明の方法を採用すれば低温で容易に前記金属塩が還元でき表面積の低下を最小限に抑えた合金化を行うことができる。

必要に応じて該金属塩中の不純物金属を抽出により除去し乾燥した後、水素中例えば 250℃で30分間前記金属塩を還元し、次いで温度をより高温に例えば 700℃に上昇させて前記還元された金属を合金化する。

白金を含む3元触媒を製造する場合には、白金を90~40原子%、第2及び第3の金属をそれぞれ5~30原子%、最も好ましくは白金50原子%、第2及び第3の金属をそれぞれ25原子%含むように

27℃で攪拌した。時間の経過に従って該混合溶液の色は黄色から橙色に変化し、更に濃い橙色になった。

約3時間経過後に室内を暗くして前記容器に電球の光を当てたところ、光の散乱が観察された。一方、触媒担体となるアセチレン・ブラック10gを100mlの純水に良く懸濁させたスラリーを前記混合溶液に加え、これを超音波攪拌機で2分間攪拌し、前記混合溶液を前記担体の細孔内に進入させるようにした。この攪拌操作では前記スラリーは懸濁したままで沈殿しなかった。

該スラリーを75~80℃のオープン中で一晚乾燥し水を除去した。このようにして得られた乾燥粉末を約200mlの蒸留水で3回洗浄して副生成物を抽出除去した。このスラリーを更に70℃で一晩乾燥して白金を担持したカーボン担体を得た。

このようにして得られた白金カーボン担体触媒のX線回折による白金の平均粒径は18Åで、透過顕微鏡による白金粒子の観察では、ほぼ均一によく揃った粒径であり、また電気化学的H<sub>2</sub>吸脱着

前記有機酸アミンの金属塩の量を調整する。

又白金を含む4元触媒を製造する場合には、白金を85~25原子%、第2、第3及び第4の金属をそれぞれ5~25原子%、最も好ましくは白金50原子%、第2及び第3の金属をそれぞれ21原子%、第4の金属を8原子%含むように前記有機酸アミンの金属塩の量を調整する。

本発明に係わる白金合金触媒は、上記した製造方法のように白金を担持させてから他の金属を担持させるだけでなく、逆に白金以外の金属を担持させ次いで白金を担持させた後に合金化して製造するようにしてもよい。

#### (実施例)

以下に本発明の実施例を記載するが、該実施例は本発明を限定するものではない。

#### 実施例1

白金1.12gを含む塩化白金酸を容量約0.5ℓの容器中の300mlの水に溶解し、該溶液に3gのNa<sub>2</sub>S<sub>2</sub>O<sub>3</sub>・5H<sub>2</sub>Oを溶解した75mlの液のうち10mlを3分掛けて滴下し、残りの65mlを一度に加え、更に

法による白金の比表面積は155ml/g、白金の担持量は10重量%であった。

酢酸マンガン(0.77ミリモル)と酢酸コバルトの水溶液50ml(0.77ミリモル)の混合溶液を使用し、該水溶液に、水酸化アンモニウム水溶液をpHが10になるまで加え5分間攪拌した。次に該酢酸アミンのマンガン塩及び酢酸アミンのコバルト塩混合水溶液に、白金のみを担持した前記カーボン担体触媒3gを加え10分間攪拌した。

その後、スラリーの乾燥、水素気流中での還元を行って前記マンガン塩及びコバルト塩をマンガン及びコバルトに還元した後、該触媒の雰囲気(900℃)に上昇させて前記白金と前記マンガン及びコバルトを合金化させた。

約3.1gの白金-マンガン-コバルト合金触媒を得ることができた。該触媒中の白金とマンガン及びコバルトの担持量を測定したところ、それぞれ0.1g/g-触媒、0.014g/g-触媒及び0.014g/g-触媒(白金50原子%、マンガン25

原子%及びコバルト25原子%)であった。

得られた白金-マンガン-コバルト合金触媒の合金粒子径を測定したところ、34Åであった。

この白金-マンガン-コバルト合金触媒を白金 0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極900mVでの活動度を測定したところ、52mA/mgPtであった。

#### 実施例2

実施例1の酢酸マンガン及び酢酸コバルトの混合水溶液に代えて、酢酸マンガンの水溶液50ml (0.77ミリモル)とギ酸ニッケルの水溶液50ml (0.77ミリモル)の混合水溶液を使用して酢酸アミンのマンガン塩及びギ酸アミンのニッケルの混合水溶液を調製したこと以外は実施例1と同一の条件で白金-マンガン-ニッケル合金触媒を得た。この触媒の合金粒子径は34Åであった。

該触媒中の白金、マンガン及びニッケルの担持量を測定したところ、それぞれ 0.1g/g-触媒、0.014g/g-触媒及び0.014g/g-触媒(白金

g-触媒、0.013g/g-触媒、0.013g/g-触媒及び 0.005g/g-触媒(白金50原子%、ニッケル21原子%、コバルト21原子%及びマンガン8原子%)であった。

この触媒を実施例1と同様に白金 0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極900mVでの活動度を測定したところ、58mA/mgPtであった。

#### 実施例4

実施例3におけるギ酸ニッケル、酢酸コバルト及び酢酸マンガンのモル量をそれぞれ0.69ミリモル、0.76ミリモル及び0.15ミリモルとしたこと以外は実施例1と同一の条件で合金触媒を調製した。この触媒の合金粒子径は35Åであった。

得られた触媒の各金属の原子%はそれぞれ白金50原子%、ニッケル22.5原子%、コバルト22.5原子%及びマンガン5原子%)であった。

この触媒を実施例1と同様に白金 0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極900mVでの活動

50原子%、マンガン25原子%及びニッケル25原子%)であった。

この触媒を実施例1と同様に白金 0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極900mVでの活動度を測定したところ、53mA/mgPtであった。

#### 実施例3

実施例1の酢酸マンガン及び酢酸コバルトの混合水溶液に代えて、ギ酸ニッケルの水溶液35ml (0.65ミリモル)、酢酸コバルトの水溶液35ml (0.65ミリモル)及び酢酸マンガンの水溶液35ml (0.25ミリモル)の混合水溶液を使用してギ酸アミンのニッケル塩、酢酸アミンのコバルト塩及び酢酸アミンのマンガン塩混合水溶液を調製したこと以外は実施例1と同一の条件で合金触媒を調製したところ、約 3.1gの白金-ニッケル-コバルト-マンガン合金触媒を得ることができた。この触媒の合金粒子径は33Åであった。

該触媒中の白金、ニッケル、コバルト及びマンガンの担持量を測定したところ、それぞれ0.1g/

度を測定したところ、54mA/mgPtであった。

#### 比較例1

酢酸マンガンの水溶液 100ml (1.74ミリモル)に、水酸化アンモニウム水溶液をpHが10になるまで加え、5分間攪拌した。次に該酢酸アミンのマンガン塩水溶液に実施例1で調製した白金カーボン担体触媒3gを加え10分間攪拌した。

その後得られたスラリーを65℃で蒸発乾燥し、次いで1ℓ/分の10%水素(残窒素)気流中 250℃で30分間還元して前記マンガン塩をマンガンに還元した後、該触媒の雰囲気を 900℃に上昇させて前記白金と前記マンガンを合金化させた(合金の平均粒子径24Å)。

容器から取り出したところ、約 3.1gの白金-マンガン合金触媒を得ることができた。化学分析法を使用して該白金-マンガン合金触媒中の白金とマンガンの担持量を測定したところ、それぞれ 0.1g/g-触媒及び0.03g/g-触媒(白金50原子%、マンガン50原子%)であった。又該触媒の合金の粒子径は24Åであった。

この白金-マンガン合金触媒とテトラフルオロエチレンの重量比が6:4になるように、白金-マンガン合金触媒とテトラフルオロエチレンのデイスパージョン液を混練し、撥水处理したカーボンシート上にこれを塗布、焼成して白金 0.5mg/cm<sup>2</sup>の電極を作製した。この電極を実施例1と同様に白金 0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極 900mVでの活動度を測定したところ、42mA/mgPtであった。

#### 比較例2及び3

実施例1における酢酸マンガン水溶液と酢酸コバルト水溶液の換わりに、(i)ギ酸ニッケル水溶液(50ml)と酢酸鉄水溶液(50ml)を(比較例2)、又は(ii)酢酸鉄水溶液(50ml)と酢酸コバルト水溶液(50ml)を(比較例3)使用して実施例1と同様にして、それぞれ白金と他の2種類の金属から成る白金合金触媒を調製した。

得られた触媒のそれぞれの金属の割合は、白金50原子%、ニッケル25原子%及び鉄25原子%(比

較例2)、及び白金50原子%、コバルト25原子%及び鉄25原子%(比較例3)であった。得られた両合金触媒を実施例1と同様に、白金 0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極900mVでの活動度を測定したところ、比較例2の白金-ニッケル-鉄合金触媒では48mA/mgPt、比較例3の白金-コバルト-鉄合金触媒では45mA/mgPtであった。

#### 比較例4及び5

比較例2と同様にして白金-ニッケル-コバルト合金触媒を調製し、比較例2と同様に活動度を測定したところ、50mA/mgPtであった。更に実施例1で調製したマンガン及びコバルトを担持する前の白金触媒の活動度を同様にして測定したところ30mA/mgPtであった。

上記した実施例及び比較例における合金触媒及び白金触媒のそれぞれの構成金属の原子%及び0.9Vにおける活動度(mA/mgPt)を表1に纏めた。

表 1

		担持され 金属	原子%	0.9V(O <sub>2</sub> )にお ける活動度 (mA/mgPt)
実施 例	1	PtCoMn	50:25:25	52
	2	PtNiMn	50:25:25	53
	3	PtNiCoMn	50:21:21:8	58
	4	PtNiCoMn	50:22.5:22.5:5	54
比 較 例	1	PtMn	50:50	42
	2	PtNiFe	50:25:25	48
	3	PtCoFe	50:25:25	45
	4	PtNiCo	50:25:25	50
	5	Pt	—	30

表1から、白金及びマンガンと、ニッケル及びコバルトの少なくとも1種から成る本発明の各実施例の合金触媒は、白金-マンガン合金触媒やマンガンを含まない他の触媒、例えば白金単独触媒より20mA/mgPt以上、白金-マンガン合金触媒より10mA/mgPt以上、又白金を含む3元合金触媒より数mA/mgPt活動度が高く、特に白金-ニッケル-コバルト-マンガンの4元合金触媒の活性度が他の実施例の触媒よりも高いことが分かる。

#### 比較例6

実施例1で得られた白金-ニッケル-マンガン合金が担持されたカーボン担体をカーバイド化用容器に入れ、窒素とメタンの1:1混合物を1ℓ/分の流速で前記容器中に供給し内温を750~770℃に維持しながら約15分間カーバイド化を行った。

得られたカーバイド化された3元白金合金触媒を実施例1と同様にして、白金0.5mg/cm<sup>2</sup>の量で熱リン酸型燃料電池のカソードとして半電池に組み、1気圧、190℃、酸素極900mVでの活動度を測定したところ、48mA/mgPtであった。

#### (発明の効果)

本発明に係わる白金合金触媒は、カーボン担体上に、(i)白金、(ii)マンガン、及び(iii)ニッケル及びコバルトの少なくとも1種を担持させて成る白金合金触媒である(請求項1)。

この白金合金触媒は、白金-マンガンの2元合金触媒や、従来の白金合金触媒としては比較的活性の高い白金-ニッケル-コバルト合金触媒より

も活性が高く、特に燃料電池用の電極触媒として使用すると有用で、その効果は各担持金属の一定割合の範囲で顕著である（請求項2）。

又本発明に係わる白金合金触媒の製造方法は、カーボン担体を白金含有イオンの溶液に浸漬し還元剤を使用して前記白金含有イオンを白金に還元して前記カーボン担体上に析出させ、該カーボン担体上に、マンガン、及びニッケル及びコバルト少なくとも1種のそれぞれの金属の有機酸アミン塩の溶液を加えかつ前記カーボン担体上の白金と合金化することを含んで成る白金合金触媒の製造方法である（請求項3）。

この製造方法によると、白金-マンガンの2元合金触媒や、従来の白金合金触媒としては比較的活性の高い白金-ニッケル-コバルト合金触媒よりも活性が高い多元白金合金触媒を得ることができる。更にマンガン等の有機酸アミン塩を使用しているため、マンガン等と既に担持されている白金との合金化を比較的低温で行うことができ、従って担持金属の凝集が抑制され表面積の大きい合

金触媒を得ることができる。使用する有機酸アミンは入手し易さ等からギ酸アミンや酢酸アミンとすることが好ましい（請求項4）。

更に前記製造方法における白金含有イオンの還元用の還元剤として還元力が弱くかつ硫黄原子を含有するチオ硫酸塩及び／又はメタ重亜硫酸塩を使用すると（請求項5）、水素化ホウ素ナトリウムのような強い還元力を有する還元剤を使用した場合と比較して、カーボン担体上に析出する金属の粒径が減少し、かつ均一な粒径の担持金属が得られる。更に還元工程中で遊離する硫黄原子に起因すると推測される成長用核が生じて金属粒子の成長するため、この傾向は一層顕著になる。従って生成するカーボン担体上の触媒金属が大きな表面積で反応物質と接触するため、その触媒比活性が高くなり前記触媒金属を有効に利用することができる。更に還元剤の還元力が小さいことから、より格子欠陥の少ない微結晶粒子が生成すると考えられ、触媒金属の粒径成長に対してより大きな耐性があり、触媒の寿命も大幅に増加する。

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PLATINUM ALLOY CATALYST AND ITS PRODUCTION PROCESS  
[Hakkin Gokin Shokubai To Sono Seizo Hoho]

Paul Stonehart, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
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## 1. Title

Platinum Alloy Catalyst and Its Production Process

## 2. Claims

(1) A platinum alloy catalyst comprising a carbon support and (i) platinum, (ii) manganese, and (iii) at least one of nickel and cobalt that are supported on the carbon support.

(2) The platinum alloy catalyst stated in Claim 1, wherein 40 to 90 atomic percent platinum, 30 to 5 atomic percent manganese, and 30 to 5 atomic percent of at least one of nickel and cobalt are supported on the carbon support.

(3) A process for preparing a platinum alloy catalyst, said process comprising immersing a carbon support in a solution of platinum-containing ions, depositing platinum on the carbon support by reducing the platinum-containing ions with the use of a reducing agent, applying a solution of an organic acid amine salt of each of the following metals, manganese and at least one of nickel and cobalt, to the carbon support, and alloying these metals with the platinum on the carbon support.

(4) The production process stated in Claim 3, wherein the organic acid amine salt is amine formate and/or amine acetate.

(5) The production process stated in Claim 3 or 4, wherein the reducing agent is a thiosulfate and/or a metabisulfite.

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\* Numbers in the margin indicate pagination in the foreign text.

### 3. Detailed Description of the Invention

#### [Field of Industrial Application]

The present invention relates to catalysts that support platinum, manganese, and other metals on a carbon support, especially to platinum alloy catalysts used as electrode catalysts for fuel cells, and it also relates to the production process thereof.

#### [Related Art and Problems Thereof]

Catalysts comprising a carbon support and various kinds of catalytic metals--mainly platinum--that are supported thereon have heretofore been employed as catalysts for various chemical reactions and for the electrodes of fuel cells. Numerous other catalysts in which other metals, such as nickel and chromium, are added to platinum for the purpose of improving catalytic performance are also known.

However, even the activity of these platinum-containing catalysts as catalysts for various types of reactions is not quite satisfactory, and there is a need for catalysts having higher activity, better yet, additionally having a longer use life.

The present inventors have proposed a platinum-containing catalyst having a long use life and also relatively high catalytic activity in which the catalytic metals supported on the carbon support have been carbonized (JP-A-H01-210035). Since, in said platinum catalyst, the supported catalytic metals are adsorbed firmly onto the support as a result of the carbonization, even when the catalyst is used in a high temperature reaction, it is highly unlikely that the

/2

bonding between the catalytic metal particles and the support becomes weak, causing said particles to migrate and aggregate with other particles, which leads to the reduction of the surface area, in other words, the reduction of the activity. As a consequence, this catalyst has an advantage in that it can maintain relatively high catalytic activity for a long period of time.

Although this catalyst has a long-enough use life, its effective surface area that serves as a catalyst is inevitably decreased because each catalytic metal is carbonized and, as a result, partially covered with carbon, and preventing said decrease requires the excessive use of an expensive metal, such as platinum or the like; consequently, this catalyst is not necessarily satisfactory from the standpoint of activity per unit cost. Attempts have been made heretofore to improve catalytic activity through the selection of metals to be supported and of the combination thereof, the attainment of a higher degree of dispersion of catalytic metals on the support so as to increase the activity per unit quantity of the supported metals, and so forth.

#### [Objectives of the Present Invention]

The present invention intends to provide platinum alloy catalysts having fully satisfactory catalytic activity by selecting a novel catalytic metal combination that has not existed heretofore and also to provide the production process thereof.

#### [Means for Solving the Problems]

A first aspect of the present invention is a platinum alloy catalyst comprising a carbon support and (i) platinum, (ii) manganese, and (iii) at least one of nickel and cobalt that are supported on the carbon support, and the second aspect thereof is a process for preparing a platinum alloy catalyst, said process comprising immersing a carbon support in a solution of platinum-containing ions, depositing platinum on the carbon support by reducing the platinum-containing ions with the use of a reducing agent, applying a solution of an organic acid amine salt of each of the following metals, manganese and at least one of nickel and cobalt, to the carbon support, and alloying these metals with the platinum on the carbon support.

The following will explain the present invention in detail.

The most distinct feature of the present invention is the addition of manganese to a catalytic metal, such as platinum or the like, so as to improve the specific activity of the catalyst.

By adding a second metal to a conventional platinum catalyst that supports platinum alone and alloying the metals, the activity of the aforesaid platinum catalyst can be improved, and appropriate selection of the second metal to be added makes it possible to achieve a dramatic activity improvement. Moreover, the addition of a third metal often leads to a further improvement of the activity. As this added metal, manganese has not been heretofore regarded as important, but the present inventors found that the addition of manganese to a carbon support that supports platinum and at least one of nickel and cobalt

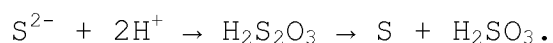
further improves the activity, thereby making it possible to provide a platinum alloy catalyst having unprecedented high activity. Based on this finding, the present invention was achieved.

In the present invention, carbon is used as the catalyst support. The term "carbon" herein is the collective designation for simple substances, such as carbon black, graphite, active carbon, and the like, that have carbon as the main component and also have any form. Preferably, the carbon support is porous and possesses a large surface area--for instance, about 30 to 2000 m<sup>2</sup>/g--and a particle size of 100 to 5000 Å or thereabouts. Acetylene black (trade name: Shawinigan Acetylene Black, Denka Black, and the like), electroconductive carbon black (trade name: Vulcan XC-72 and the like), and graphitized carbon black, for example, may be employed. It is conjectured that, because the support in the present invention is carbon, each catalytic metal's support-facing part, which does not take part in the catalytic reaction, interacts with the carbon support and, as a result, is subjected to an action similar to carbonization in the high temperature atmosphere of the later-described alloying process, thereby bonding strongly with the aforesaid carbon support and consequently yielding the effect of inhibiting aggregation.

According to the process of this invention, first of all, platinum metal is supported on the aforesaid carbon support. As the method for supporting the platinum metal, a conventional method that impregnates the aforesaid carbon support with a solution of platinum-

containing ions--for example, an aqueous solution of chloroplatinic acid--and reduces the platinum-containing ions, thereby depositing platinum metal onto the carbon support, can be employed as is. If, however, a strong reducing agent is used in said reduction reaction, the size of the generated platinum particles increases, and the /3 surface area of the particles per unit weight considerably decreases. For this reason, it is preferable to use a weak reducing agent, such as thiosulfate or sodium salt thereof ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) so as to suppress the decrease of the platinum surface area. Said thiosulfate or its sodium salt reacts with chloroplatinic ions, that is, the aforesaid platinum-containing ions, in the aqueous solution and forms a finely divided metal sol having a large surface area.

In the reaction that employs sodium thiosulfate, a very finely divided sulfur sol that is formed by decomposition of a sulfur compound, which is known to occur in an acidic solution, is believed to be generated according to the following formula:



The sulfur particles thus formed serve as nuclei for growing very finely divided metal catalyst particles. Accordingly, it is preferable to slowly add, that is, to add drop by drop, the initial several milliliters of the sodium thiosulfate solution and then to add the rest of the solution all at once so as to ensure the formation of the nuclei for growing use.

As the reaction progresses, the solution turns from yellow to orange, and, as the fine metal crystals grow over the course of several hours, the color of the solution gradually becomes darker. The light passing through the solution exhibits the Tyndall effect, which indicates the presence of colloidal particles.

This sol is adsorbed onto the carbon support and then subjected to appropriate procedures, such as drying and the like, thereby obtaining a carbon support on which is supported platinum.

More specifically, when the aforesaid solution becomes nearly opaque, the aforesaid carbon support is added thereto, and the slurry thus formed is agitated with, for example, an ultrasonic agitator so as to cause the liquid phase to penetrate into the pores of the aforesaid carbon support. A thicker slurry is formed by this procedure, which remains suspended and seldom precipitates. Drying this slurry at, for example, 75 to 80 °C for 1 to 3 days and thereby removing water yields a dry powder containing a salt of a reaction by-product. The by-product can be dissolved and eliminated by extracting the dried catalyst several times with, for instance, 100 to 200 mL distilled water. In the case in which the support is graphitized carbon black, the aforesaid slurry precipitates; therefore, the catalyst can be separated from the aqueous phase by discarding the aqueous phase. After this procedure is repeated several times, the catalyst is dried overnight at about 110 °C.



The catalyst thus prepared has a large surface area. Reacting, for example, a chloroplatinic acid aqueous solution having a concentration of about 1 g/100 mL with a sodium thiosulfate (pentahydrate) aqueous solution having a concentration of about 3 g/75 mL according to this process yields a catalyst that supports platinum having a uniform particle size and a specific surface area of approximately 148 m<sup>2</sup>/g.

In place of the above procedures, a slurring-filtration-washing process can be utilized. This process is applicable to catalysts that do not precipitate readily, as is the case with acetylene black.

It is believed that, because the thermodynamic driving force of the reaction between the chloroplatinic acid ions and the thiosulfate ions is smaller than that of the conventional art and, consequently, fine crystal particles with fewer defects are produced, the catalyst particles produced in this process are more resistant against the grain growth that causes the surface area of platinum to decrease as the use time increases. Fine particles having a uniform particle size of 20 Å or smaller can be obtained by the aforesaid reaction of thiosulfate and chloroplatinic acid.

In addition to the aforesaid sodium thiosulfate, the relatively weak reducing agent that can be used in the present invention includes sodium metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) and the like.

Up to this point, the process that impregnates the carbon support used in the present invention with a platinum-containing solution and

subsequently reduces platinum-containing ions has been described in detail, but the platinum alloy catalyst pertaining to the present invention may be a catalyst that is produced instead by reducing the platinum-containing ions prior to the impregnation, and this process also yields catalyst particles having high dispersibility.

Next, metals other than platinum, that is, manganese and at least one of cobalt and nickel, are supported on the platinum-supporting carbon support, and the platinum and the other metals are alloyed by heating, but, because conducting this alloying at high temperature causes the resulting alloy to aggregate and have a reduced surface area, it is not desirable to employ an ordinary alloying method here. For this reason, according to the process of the present invention, ammonium hydroxide is initially added to a warm aqueous solution of organic acid salts--preferably formates or acetates--of metals to be added to the platinum, that is, manganese, cobalt, and/or nickel, thereby converting the acid salts into the corresponding metal salts /4 of the organic acid amine--preferably the metal salts of amine formate or amine acetate.

When an ordinary metal salt (for example, nitrate or the like) is heat-treated, a heat-resistant oxide is formed, and it requires high-temperature reduction for alloying it with platinum; as a result, before the platinum is alloyed, crystal growth (decrease of the surface area) occurs. On the other hand, by the process of this invention, the aforesaid metal salts can be reduced easily at a

relatively low temperature, thus making it possible to conduct the alloying with a minimum decrease of the surface area.

After, if necessary, impure metals in the metal salts are removed by extraction and the metal salts are dried, the metal salts are reduced in hydrogen at, for example, 250 °C for 30 minutes, after which the temperature is raised to a higher temperature, for example, to 700 °C, at which temperature the reduced metals are alloyed.

In the case of preparing a ternary catalyst containing platinum, the quantities of the organic acid amine metal salts are so adjusted that the resulting catalyst contains 90 to 40 atomic percent platinum and 5 to 30 atomic percent each of the second and third metals--most desirably, 50 atomic percent platinum and 25 atomic percent each of the second and third metals.

In the case of preparing a quaternary catalyst containing platinum, the quantities of the organic acid amine metal salts are so adjusted that the resulting catalyst contains 85 to 25 atomic percent platinum and 5 to 25 atomic percent each of the second, third, and fourth metals--most desirably, 50 atomic percent platinum, 21 atomic percent each of the second and third metals, and 8 atomic percent of the fourth metal.

The platinum alloy catalyst pertaining to the present invention may be prepared not only by supporting platinum before supporting the other metals, as in the aforesaid production process, but, instead, by

supporting platinum after supporting the other metals and subsequently by alloying them.

[Working Examples]

The following will describe working examples of the present invention, but these working examples are not intended to limit the scope of the present invention.

Working Example 1

Chloroplatinic acid containing 1.12 g platinum was dissolved in 300 ml water contained in an approximately 0.5 L-capacity vessel. To said solution was added 10 mL out of 75 mL of a solution in which was dissolved 3 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  drop by drop over the course of 3 minutes, and the remaining 65 ml was added all at once, after which the solution was stirred at 27 °C. With the passage of time, the mixture solution turned from yellow to orange and then to dark orange.

After the passage of about 3 hours, the room was darkened, and, when the light of an electric bulb was applied to the vessel, scattering of the light was observed. Meanwhile, 10 g acetylene black, which would serve as the catalyst support, was suspended in 100 mL pure water to prepare a well suspended slurry, which was then added to the above mixture solution. This was stirred for 2 minutes with an ultrasonic agitator so as to cause the mixture solution to penetrate into the pores of the support. During this stirring operation, the slurry remained suspended and did not precipitate.

The slurry was dried in an oven at 75 to 80 °C overnight, thereby eliminating water. The dry powder thus obtained was washed three times with approximately 200 mL distilled water, thereby extracting and eliminating by-products. This slurry was further dried overnight at 70 °C, thereby obtaining a platinum-supporting carbon support.

The average particle size of the platinum of the platinum-carbon support catalyst thus obtained was 18 Å, as measured by X-ray diffraction, and the platinum particles were found to have a nearly uniform particle size as a result of the observation with a transmission electron microscope. The specific surface area was 155 m<sup>2</sup>/g, and the amount of the supported platinum was 10 percent by weight, as measured by an electrochemical H<sub>2</sub> adsorption/desorption method.

To a mixed solution of 50 mL (0.77 mmol) of a manganese acetate aqueous solution and of 50 mL (0.77 mmol) of a cobalt acetate aqueous solution was added an ammonium hydroxide aqueous solution until the pH of the solution reached 10, and the solution was stirred for 5 minutes. Next, to the mixed aqueous solution of a manganese salt of amine acetate and a cobalt salt of amine acetate was added 3 g of the aforesaid carbon support catalyst, which supported platinum alone, and the solution was stirred for 10 minutes.

Thereafter, the slurry was dried, and the manganese salt and the cobalt salt were reduced to manganese and cobalt by reducing the slurry in a hydrogen flow, after which the temperature of the

atmosphere of the catalyst was raised to 900 °C so as to alloy the aforesaid platinum, manganese, and cobalt.

Approximately 3.1 g of a platinum-manganese-cobalt alloy catalyst was obtained. The supported quantities of the platinum, manganese, and cobalt in said catalyst were measured and found to be 0.1 g/g-catalyst, 0.014 g/g-catalyst, and 0.014 0.014 [sic] g/g-catalyst (platinum: 50 atomic percent, manganese: 25 atomic percent, and cobalt: 25 atomic /5 percent), respectively.

The particle size of the alloy particles of the platinum-manganese-cobalt alloy catalyst thus obtained was measured and found to be 34 Å.

This platinum-manganese-cobalt alloy catalyst was incorporated into a half cell in a quantity of 0.5 mg platinum/cm<sup>2</sup> as the cathode of a hot phosphoric acid fuel cell, and its activity was measured under 1 atm at 190 °C and 900 mV at the oxygen electrode and found to be 52 mA/mg-Pt.

#### Working Example 2

A platinum-manganese-nickel alloy catalyst was prepared under the same conditions as those in Working Example 1, except that, in place of the mixed aqueous solution of manganese acetate and cobalt acetate used in Working Example 1, a mixed aqueous solution of 50 mL (0.77 mmol) of a manganese acetate aqueous solution and of 50 mL (0.77 mmol) of a nickel formate aqueous solution was used to prepare a mixed aqueous solution of a manganese salt of amine acetate and a nickel

salt of amine formate. The alloy particle size of this catalyst was 34 Å.

The supported quantities of the platinum, manganese, and nickel in the catalyst were measured and found to be 0.1 g/g-catalyst, 0.014 g/g-catalyst, and 0.014 g/g-catalyst (platinum: 50 atomic percent, manganese: 25 atomic percent, and nickel: 25 atomic percent).

This catalyst, as in Working Example 1, was incorporated into a half cell in a quantity of 0.5 mg platinum/cm<sup>2</sup> as the cathode of a hot phosphoric acid fuel cell, and its activity was measured under 1 atm at 190 °C and 900 mV at the oxygen electrode and found to be 53 mA/mg-Pt.

### Working Example 3

A platinum-nickel-cobalt-manganese alloy catalyst was prepared under the same conditions as those in Working Example 1, except that, in place of the mixed aqueous solution of manganese acetate and cobalt acetate of Working Example 1, a mixed aqueous solution of 35 mL (0.65 mmol) of a nickel formate aqueous solution, 35 mL (0.65 mmol) of a cobalt acetate aqueous solution, and 35 mL (0.25 mmol) of a manganese acetate aqueous solution was used to prepare a mixture aqueous solution of a nickel salt of amine formate, a cobalt salt of amine acetate, and a manganese salt of amine acetate. As a result, approximately 3.1 g of said catalyst was obtained. The alloy particle size of this catalyst was 33 Å.

The supported quantities of the platinum, nickel, cobalt, and manganese in the catalyst were measured and found to be 0.1 g/g-catalyst, 0.013 g/g-catalyst, 0.013 g/g-catalyst, and 0.005 g/g-catalyst (platinum: 50 atomic percent, nickel: 21 atomic percent, cobalt: 21 atomic percent, and manganese: 8 atomic percent), respectively.

This catalyst, as in Working Example 1, was incorporated into a half cell in a quantity of 0.5 mg platinum/cm<sup>2</sup> as the cathode of a hot phosphoric acid fuel cell, and its activity was measured under 1 atm at 190 °C and 900 mV at the oxygen electrode and found to be 58 mA/mg-Pt.

#### Working Example 4

An alloy catalyst was prepared under the same conditions as those in Working Example 1, except that the molar quantities of the nickel formate, cobalt acetate, and manganese acetate in Working Example 3 were changed to 0.69 mmol, 0.76 mmol, and 0.15 mmol, respectively. The alloy particle size of this catalyst was 35 Å.

The atomic percents of the metals of the obtained catalyst were 50 atomic percent for the platinum, 22.5 atomic percent for the nickel, 22.5 atomic percent for the cobalt, and 5 atomic percent for the manganese.

This catalyst, as in Working Example 1, was incorporated into a half cell in a quantity of 0.5 mg platinum/cm<sup>2</sup> as the cathode of a hot phosphoric acid fuel cell, and its activity was measured under 1 atm



at 190 °C and 900 mV at the oxygen electrode and found to be 54 mA/mg-Pt.

#### Comparative Example 1

To 100 mL (1.74 mmol) of an aqueous solution of manganese acetate was added an ammonium hydroxide aqueous solution until the pH of the solution reached 10, and the solution was stirred for 5 minutes. Next, to the aqueous solution of a manganese salt of amine acetate was added 3 g of the platinum-carbon support catalyst prepared in Working Example 1, and the solution was stirred for 10 minutes.

Thereafter, the slurry thus obtained was dried at 65 °C by evaporation and reduced in a 10 percent hydrogen flow (the balance being nitrogen) at a rate of 1 liter/minute at 250 °C for 30 minutes, thereby reducing the manganese salt to manganese, after which the temperature of the atmosphere of the catalyst was raised to 900 °C, thereby alloying the platinum and the manganese (the average particle size of the alloy was 24 Å).

Approximately 3.1 g of a platinum-manganese alloy catalyst was found to be obtained when it was taken out from the vessel. The supported quantities of the platinum and manganese in the platinum-manganese alloy catalyst were measured by a chemical analysis method and found to be 0.1 g/g-catalyst and 0.03 g/g-catalyst (platinum: 50 atomic percent, manganese: 50 atomic percent), respectively. The alloy particle size of the catalyst was found to be 24 Å.

This platinum-manganese alloy catalyst and a dispersion liquid of /6

tetrafluoroethylene were kneaded so as to set the weight ratio of the platinum-manganese alloy catalyst and the tetrafluoroethylene to 6 : 4. This mixture was applied to a carbon sheet that had been subjected to a water repellent treatment, and the sheet was baked, thereby preparing an electrode having 0.5 mg/cm<sup>2</sup> platinum. This electrode, as in Working Example 1, was incorporated into a half cell in a quantity of 0.5 mg platinum/cm<sup>2</sup> as the cathode of a hot phosphoric acid fuel cell, and its activity was measured under 1 atm at 190 °C and 900 mV at the oxygen electrode and found to be 42 mA/mg-Pt.

#### Comparative Examples 2 and 3

In place of the manganese acetate aqueous solution and the cobalt acetate aqueous solution in Working Example 1, (i) a nickel formate aqueous solution (50 mL) and a ferrous acetate aqueous solution (50 mL) (Comparative Example 2) or (ii) a ferrous acetate aqueous solution (50 mL) and a cobalt acetate aqueous solution (50 mL) (Comparative Example 3) were used, and two platinum alloy catalysts, each comprising platinum and two other kinds of metals, were prepared in a manner similar to Working Example 1.

The proportions of the individual metals of the catalyst thus obtained were 50 atomic percent platinum, 25 atomic percent nickel, and 25 atomic percent iron (Comparative Example 2), and 50 atomic percent platinum, 25 atomic percent cobalt, and 25 atomic percent iron (Comparative Example 3). Both catalysts thus obtained, as in Working Example 1, were incorporated into half cells at a rate of 0.5 mg

platinum/cm<sup>2</sup> as the cathode of hot phosphoric acid fuel cells, and their activities were measured under 1 atm at 190 °C and 900 mV at the oxygen electrode and found to be 48 mA/mg-Pt for the platinum-nickel-iron alloy catalyst prepared in Comparative Example 2 and 45 mA/mg-Pt for the platinum-cobalt-iron alloy catalyst prepared in Comparative Example 3.

#### Comparative Examples 4 and 5

A platinum-nickel-cobalt alloy catalyst was prepared in a manner similar to Comparative Example 2, and the activity was measured similarly to Comparative Example 2 and found to be 50 mA/mg-Pt. Furthermore, the activity of the platinum catalyst prepared in Working Example 1 was similarly measured prior to the supporting of manganese and cobalt and found to be 30 mA/mg-Pt.

The atomic percents of the constituent metals of the alloy catalysts and platinum catalyst in the aforesaid working examples and comparative examples and the activity (mA/mg-Pt) thereof at 0.9 V are summarized in Table 1.

TABLE 1

		担持され 金属 (c)	原子% (d)	0.9V(O <sub>2</sub> )にお ける活動度(e) (mA/mgPt)
(a) 実 施 例	1	PtCoRu	50:25:25	52
	2	PtNiRu	50:25:25	53
	3	PtNiCoRu	50:21:21:8	58
	4	PtNiCoRu	50:22.5:22.5:5	54
(b) 比 較 例	1	PtRu	50:50	42
	2	PtNiFe	50:25:25	48
	3	PtCoFe	50:25:25	45
	4	PtNiCo	50:25:25	50
	5	Pt	—	30

Key: a) working examples; b) comparative examples; c) supported metals; d) atomic %; e) activity at 0.9 V (O<sub>2</sub>)

As is evident from Table 1, the activities of the alloy catalysts of the working examples of the present invention, which comprise platinum, manganese, and at least one of nickel and cobalt, are higher than those of the platinum-manganese alloy catalyst and the other catalysts that did not contain manganese--for example, higher than that of the catalyst containing only platinum by 20 mA/mg-Pt or more, higher than that of the platinum-manganese catalyst by 10 mA/mg-Pt or more, and higher than that of the platinum-containing ternary catalysts by several mA/mg-Pt. It can also be seen that the platinum-nickel-cobalt-manganese quaternary alloy catalyst, in particular, has a higher activity than those of the other working examples.

#### Comparative Example 6

After the carbon support obtained in Working Example 1, which supported a platinum-nickel-manganese alloy, was put in a vessel for carbonization use, it was carbonized for about 15 minutes while a 1:1 mixture of nitrogen and methane was supplied into the vessel at a flow rate of 1 liter/minute and the internal temperature was maintained at 750 to 770 °C.

This carbonized ternary platinum alloy catalyst, as in Working Example 1, was incorporated into a half cell in a quantity of 0.5 mg platinum/cm<sup>2</sup> as the cathode of a hot phosphoric acid fuel cell, and its activity was measured under 1 atm at 190 °C and 900 mV at the oxygen electrode and found to be 48 mA/mg-Pt.

[Effects of the Invention]

The platinum alloy catalyst pertaining to the present invention is a platinum catalyst alloy comprising a carbon support and (i) platinum, (ii) manganese, and (iii) at least one of nickel and cobalt that are supported on the carbon support (Claim 1).

This platinum alloy catalyst has a higher activity than platinum-manganese binary alloy catalysts and even a higher activity than platinum-nickel-cobalt alloy catalysts, which have a relatively higher /7 activity among conventional platinum alloy catalysts, and it is especially effective when used as an electrode catalyst for fuel cell use. Its effects are prominent when each of the supported metals is within a certain percentage range (Claim 2).

The platinum alloy catalyst production process pertaining to the present invention is a platinum alloy catalyst production process comprising immersing a carbon support in a solution of platinum-containing ions, depositing platinum on the carbon support by reducing the platinum-containing ions with the use of a reducing agent, applying a solution of an organic acid amine salt of each of the following metals, manganese and at least one of nickel and cobalt, to the carbon support, and alloying these metals with the platinum on the carbon support (Claim 3).

This production process can yield multicomponent alloys that have a higher activity than platinum-manganese binary alloy catalysts and even a higher activity than platinum-nickel-cobalt alloy catalysts,

which have a relatively higher activity among conventional platinum alloy catalysts. Furthermore, because organic acid amine salts of manganese and the like are used, alloying of manganese and the like and the already supported platinum can be effected at a relatively low temperature, thus inhibiting the aggregation of the supported metals; as a consequence, an alloy catalyst having a large surface area can be obtained. The organic acid amine used here is preferably amine formate or amine acetate due to their high availability (Claim 4.)

Further, if a thiosulfate and/or metabisulfite, which have a weak reducing power and contain sulfur atoms, is used as the reducing agent for the reduction of the platinum-containing ions in the aforesaid production process (Claim 5), the particle size of the metals deposited on the carbon support becomes smaller, and supported metals having a more uniform particle size can be obtained, compared to the case of using a reducing agent having a strong reducing power, such as sodium borohydride or the like. Furthermore, these tendencies become more prominent because the growth-use nuclei, which are conjectured to be attributed to the sulfur atoms that are released in the reduction process, are formed and facilitate the growth of metal particles. Therefore, the catalytic metals formed on the carbon support make contact with a reaction substance over a large surface area; as a consequence, the catalytic specific activity increases, and the aforesaid catalytic metals can be utilized efficiently. In addition, because the reducing power of the reducing agent is small, fine

crystal particles having fewer lattice defects are believed to be grown, thus exhibiting a higher resistance against the grain growth of the catalytic metals; consequently, the use life of the catalyst is dramatically extended.